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E. A. Benham^a; P. D. Smith^a; E. T. Hsieh^a; M. P. McDaniel^a

^a Phillips Research Center, Bartlesville, Oklahoma

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MIXED ORGANO/OXIDE CHROMIUM POLYMERIZATION CATALYSTS

E. A. BENHAM, P. D. SMITH, E. T. HSIEH, and M. P. McDANIEL

Phillips Research Center
Bartlesville, Oklahoma 74004

ABSTRACT

Supported chromium oxide catalysts are activated by calcination in dry air at 400-900°C, which dehydrates the carrier and binds chromium(VI) to the surface. A reduction by ethylene then provides the active species. Alternatively, the carrier can be calcined alone and afterward impregnated with an organochromium compound. Both procedures can produce an active catalyst for ethylene polymerization, but the two types differ considerably in their behavior. A third type is made by reacting an organochromium compound with the activated chromium oxide catalyst. This "mixed" catalyst displays some of the characteristics of both parents, but is not a simple combination of the two.

INTRODUCTION

The traditional Phillips polymerization catalyst, discovered by Hogan and Banks in the early 1950s [1] and still a mainstay of commercial polyethylene production, consists of chromium(VI) oxide supported on silica. A chromium compound, typically CrO_3 , is impregnated onto the silica which is then calcined in dry air at 400°C or higher. The calcining step binds the chromium to the support, probably through an esterification with surface hydroxyls to create a surface Cr(VI) species. This material is a strong oxidizing agent and reacts with ethylene to form the active catalyst.

Lower valent organochromium compounds also form active polymerization catalysts when anchored to a carrier. Walker and Czenkusch [2] discovered in

the early 1960s that diarene chromium(0) compounds polymerized ethylene when impregnated onto silica-alumina. Dozens of other organochromium (organo-Cr) species have also been found to be active [3-8]. Although these compounds differ widely, for example, the valence may be 0, 1, 2, 3, or 4, we lump them together here as a group because in general they behave more like each other than like the chromium oxide (Cr oxide) based catalysts. Unlike Cr oxide, they produce branched polymers of extremely broad molecular weight distribution.

This report compares some of the main characteristics of the two families of supported chromium catalysts, and also describes a third type. It is possible to prepare a mixed Cr-organo/oxide catalyst by reducing the Cr(VI) oxide, not with ethylene, as is usually done, but with a lower valent organo-Cr compound, producing, no doubt, some highly complex surface chromium species [8, 9]. Such hybrid catalysts are highly active, often more so than either of the starting components, and possess some of the useful characteristics of both parents.

EXPERIMENTAL

The catalyst supports used in this study were all of high porosity, suitable for polymerization catalysts. Aluminophosphates were prepared by the coprecipitation of aluminum and phosphate ions, as previously described [10]. Davison grade 952 silica was used, having a total porosity of $1.6 \text{ cm}^3/\text{g}$ and a surface area of about $280 \text{ m}^2/\text{g}$. The alumina was Ketjen grade B, having a similar pore volume and a surface area near $350 \text{ m}^2/\text{g}$. Chromium-oxide-based catalysts were prepared by impregnating these supports with an alcoholic solution of chromium(III) acetate to equal 1 wt% Cr and drying overnight under vacuum.

To activate the catalyst or support, about 10 g was fluidized in a dry air stream for 3 h at $250\text{-}800^\circ\text{C}$, as specified for each experiment. A quartz tube was used with a sintered glass disk to support the sample [10]. This converts chromium into the hexavalent state.

Organochromium and mixed catalysts were prepared by slurring about 5 g of the calcined support in dry heptane. The organochromium compound was then added to make the resultant catalyst about 1 wt% Cr. Usually, all of the chromium was adsorbed onto the support. Any unadsorbed Cr was rinsed away by three pentane washes, then the excess pentane was evaporated at $<50^\circ\text{C}$.

In the preparation and handling of organochromium compounds, all opera-

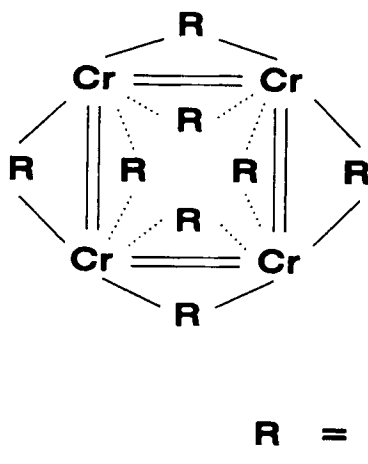


FIG. 1. Unusual structure of octakis(μ -trimethylsilylmethyl)tetrachromium(II), $\text{Cr}_4(\text{TMSM})_8$.

tions were conducted under a nitrogen atmosphere. Solvents were freshly distilled from calcium hydride or Na/benzophenone under nitrogen, or in some cases they were passed through a CO-reduced Cr/silica column. One compound used extensively throughout this report was octakis(μ -trimethylsilylmethyl)tetrachromium(II), abbreviated $\text{Cr}_4(\text{TMSM})_8$. It has an unusual four-centered planar structure, with Cr—Cr bonding and bridging TMSM ligands above and below the plane. Each chromium probably has agostic hydrogen bonding to one ligand. It was prepared as previously described [8], and the structure is pictured in Fig. 1. Another organo-Cr compound used commonly, bis(dimethylpentadienyl)chromium(II), or $\text{Cr}(\text{DMPD})_2$, was made according to Ref. 11. Chromocene, $\text{Cr}(\text{C}_5\text{H}_5)_2$, was purchased from Strem Chemical Company and used without further purification. Dicumene-Cr(0) was obtained from Aldrich Chemical Company. $\text{Cr}(\text{mesitylene})_2$ was made according to Ref. 12.

Ethylene polymerization was conducted under slurry conditions at 95°C in a 2-L stirred autoclave, as previously described [13]. Most organo-Cr catalysts were run with ~ 0.7 atm hydrogen in the reactor. Size-exclusion chromatography (SEC) on the polymer was done at 140°C on a Waters Model 150 GPC equipped with infrared detector. The solution concentration, 0.25% polymer in 1,2,4-trichlorobenzene, was chosen to give reasonable elution times.

RESULTS AND DISCUSSION

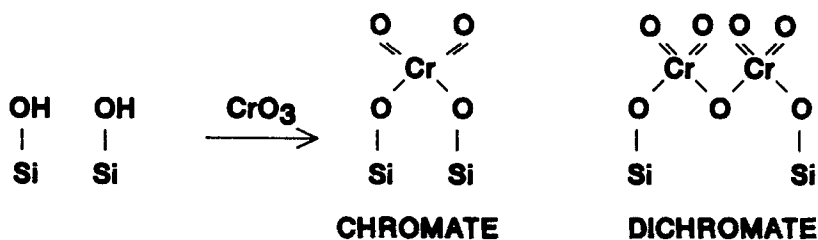
Chromium Oxide Catalysts

Almost any chromium compound can be impregnated onto silica to form the Phillips Cr(VI) oxide catalyst because the chromium is converted to the hexavalent form during calcination in air. The silica is more than just an inert carrier; it also stabilizes the hexavalent oxide against thermal decomposition [14]. If the support is overloaded with CrO_3 , the excess decomposes during calcining to the trivalent oxide Cr_2O_3 , which is inactive [15]. After the calcining step, the chromium is usually envisioned as a surface chromate, or perhaps dichromate, species, both of which are attached to the support through two oxide links [14-18] (Scheme 1).

On contact with ethylene the hexavalent surface species is reduced to a lower valence, we believe to Cr(II), although other researchers argue for Cr(III) or Cr(V) [3, 19, 20]. Polymerization starts after a brief induction time (shown in Fig. 2) which corresponds to the reduction. Thereafter, the rate gradually increases with time. Alternatively, the catalyst may be pre-reduced by carbon monoxide at 350°C before contact with ethylene to yield Cr(II). This often eliminates the induction time. Chemisorption studies suggests the existence of several types of Cr(II) species that differ in the extent to which they are coordinatively unsaturated [3]. Thus, not all of the Cr is active; some seems to be coordinated to surface oxides.

Surface hydroxyls which survive the calcining step may likewise interfere with polymerization, perhaps also by coordinating to the active site [21]. Thus, the activity of the catalyst improves with calcining temperature, at least up to about $900\text{-}1000^\circ\text{C}$, where the silica begins to sinter (Fig. 3).

After reduction the chromium site becomes alkylated, i.e., the first polymer chain starts growing, by a process that is not well understood [3]. The



SCHEME 1.

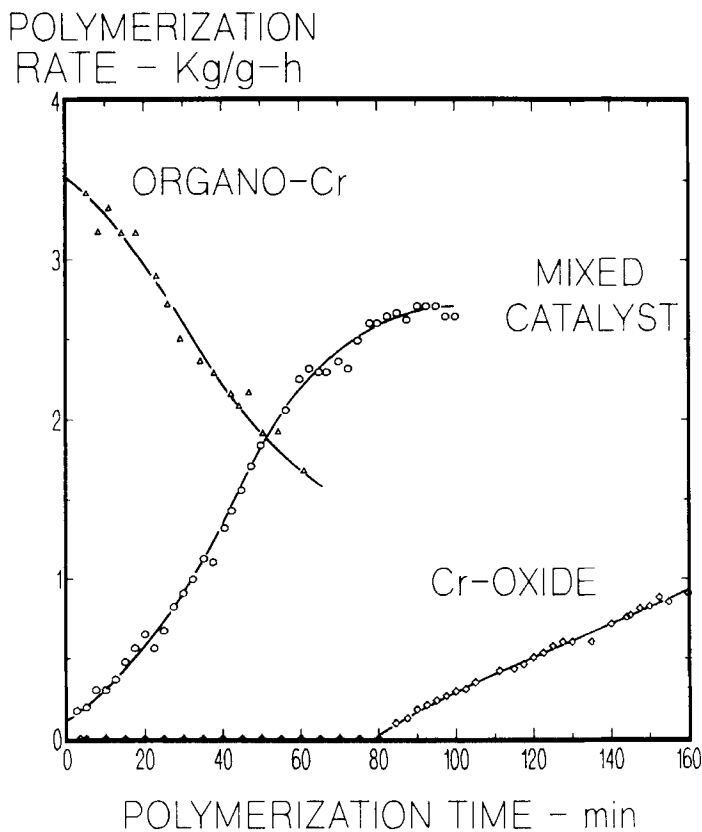


FIG. 2. Typical kinetic profile of the three types of catalysts. Cr-oxide: Cabosil silica containing 1% Cr calcined at 800°C. Organo-Cr: $\text{Cr}_4(\text{TMSM})_8$ on fluorided alumina. Mixed catalyst: Above Cr oxide/Cabosil treated with $\text{Cr}_4(\text{TMSM})_8$.

alkylation may be responsible for the gradual rise in polymerization rate seen in Fig. 2. Even CO-reduced catalysts often exhibit this slow rise in rate.

Chain transfer, the termination of one chain and the initiation of its successor on the same active site, is a continuous part of the polymerization process, occurring several times per second [3, 14]. A hydrogen atom on the beta carbon of the chain is thought to shift to monomer. This would account for the fact that each chain has a terminal vinyl on one end and a methyl on the other.

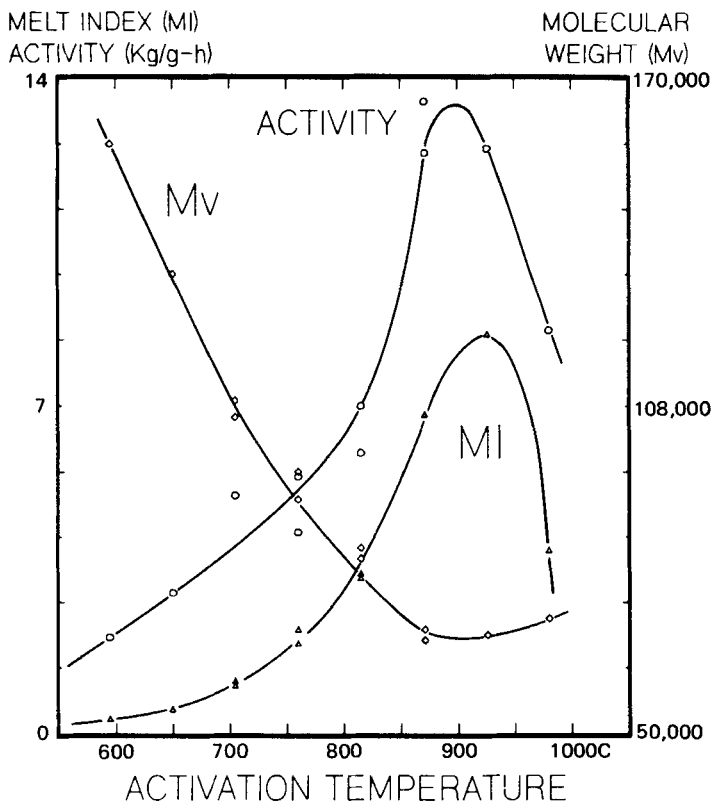
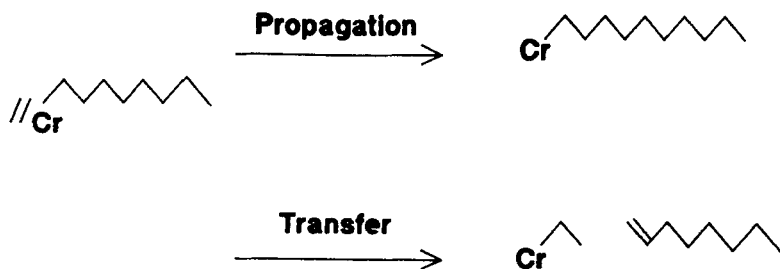


FIG. 3. The activity of Cr oxide/silica as a function of calcination temperature. The activity increases up to the point where the catalyst sinters. Chain transfer is similarly enhanced, as shown by the increasing melt index (MI) and decreasing viscosity-average molecular weight (\bar{M}_v) of the polymer produced.



SCHEME 2.

Thus, the chain length is determined by the relative rates of propagation and termination (Scheme 2).

Chain transfer is especially sensitive to the calcining history of the catalyst. Figure 3 shows that the molecular weight (MW) of the polymer decreases as the catalyst becomes more dehydroxylated at the higher calcining temperatures. Perhaps coordination to hydroxyls somehow retards the termination mechanism. Many other factors also influence the chain transfer rate on a catalyst, such as catalyst additives [22-25], reactor temperature [3], and monomer type and concentration [3, 14, 19]. Hydrogen, which is used with Ziegler catalysts to regulate MW, has very little effect on Cr oxide/silica.

The transfer rate and propagation rate are no doubt affected by the local electronic environment at each site. Thus, on a heterogeneous catalyst surface like silica, where site environment can vary considerably, the average MW of the polymer produced by each site can also vary among sites. The MW distribution then becomes a measure of site heterogeneity. Cr oxide/silica tends to produce a narrow to moderate MW distribution with weight/number ratios (\bar{M}_w/\bar{M}_n) of 4 to 15, whereas a uniform population of sites should produce $\bar{M}_w/\bar{M}_n = 2$ [3, 19, 26, 27]. A typical size-exclusion chromatogram of polymer from Cr oxide/silica is shown in Fig. 4.

Polyethylene chains produced over Cr oxide/silica catalysts are almost entirely linear when prepared at the relatively high ethylene concentrations which are typical of commercial processes. Branching is obtained by copolymerizing another monomer such as 1-hexene with the ethylene. Branches tend to break up the crystalline order of the polymer, thereby lowering its density. The stiffness of the resin, measured by the flexural modulus, tends to parallel the density as shown in Fig. 5.

Other polymer properties, such as environmental stress crack resistance and impact or tear resistance, are also influenced by the amount and type of branching, and by the branch location. The elasticity of the molten polymer (how it swells and flows) seems to be more related to the MW distribution. On the whole, Cr oxide/silica catalysts produce resin with an excellent combination of these properties for commercial blow molding, film, and pipe applications.

Organochromium Catalysts

Organochromium compounds, although not usually active in themselves [3-6], become active polymerization catalysts when deposited on an oxide support. However, they often behave quite differently from Cr oxide catalysts, probably because they attach to the carrier in a different way: Cr oxide is tightly held to the surface by two links, but the organo-Cr compounds prob-

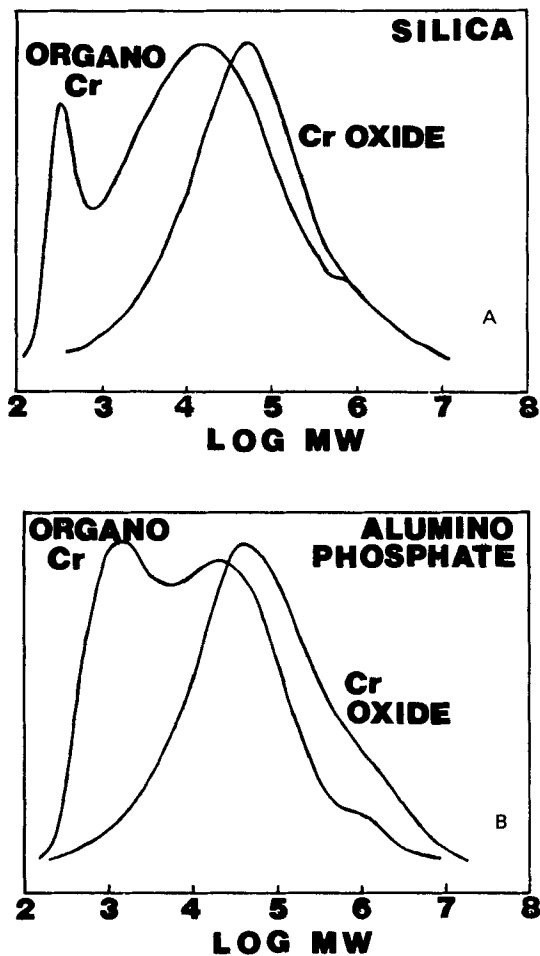


FIG. 4. Size-exclusion chromatograms of polymers from Cr-oxide and organo-Cr on two supports. (A) Cr oxide/silica and $\text{Cr}(\text{DMPD})_2/\text{silica}$; (B) Cr-oxide/ AlPO_4 and $\text{Cr}(\text{DMPD})_2/\text{AlPO}_4$. The organo-Cr catalysts often produce two or more SEC peaks, which may result from reaction of the Cr with different surface sites.

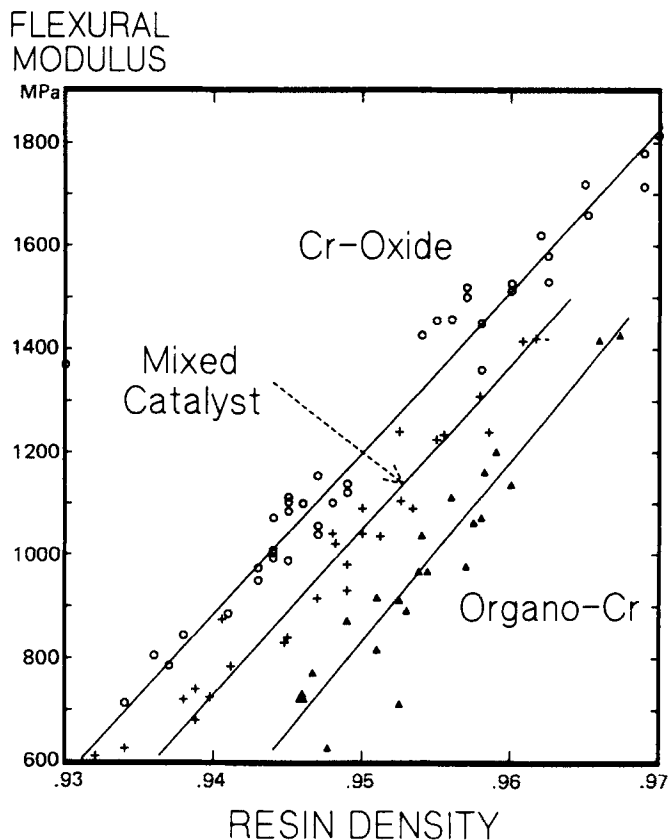
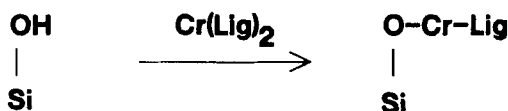


FIG. 5. Stiffness/density relationship for polymers from the three types of catalysts. The organo-Cr catalysts produce resins that are less stiff for a certain density. Upper line: Cr oxide/silica. Lower line: $\text{Cr}(\text{CUM})_2$, $\text{Cr}(\text{DMPD})_2$, and $\text{Cr}_4(\text{TMSM})_8$ on various carriers. Middle line: $\text{Cr}_4(\text{TMSM})_8$ on Cr oxide/silica.

ably attach through only one. The carrier is first calcined to dehydrate the surface, leaving mainly isolated single hydroxyls. Then, on contact with the organo-Cr compound, these react to release one of the ligands and bind the Cr through a single oxide link (Scheme 3).



SCHEME 3.

Thus Karol et al. showed that chromocene, $\text{Cr}(\text{C}_5\text{H}_5)_2$, reacts with calcined silica to release one C_5H_6 per Cr [6]. Likewise, propylene is released upon deposition of $\text{Cr}(\text{allyl})_2$ and $\text{Si}(\text{CH}_3)_4$ by $\text{Cr}_4(\text{TMSM})_8$ [3]. Bisarene $\text{Cr}(\text{O})$ acts a little differently in that H_2 is released, suggesting an oxidation on binding, perhaps to $\text{Cr}(\text{I})$ [3]. The valence of the organo-Cr compounds can vary from $\text{Cr}(\text{O})$ to $\text{Cr}(\text{IV})$, but in general they behave more like each other than like the oxide.

The activity of the organo-Cr compound is often enhanced if the hydroxyl group contains some acidic character. This is particularly true of dicumene $\text{Cr}(\text{O})$ which has no activity when deposited at 50°C onto silica [28]. However, the silica can be "activated" by impregnating it with other ingredients, such as aluminum or a phosphating treatment, before calcination. Some examples are shown in Table 1. Even sulfuric acid seems to activate the silica to a small degree, and other metals, such as bismuth, also provide limited activity.

TABLE 1. Catalyst Activity: Dicumene $\text{Cr}(\text{O})$
Deposited onto Calcined Silicas

Carrier	Activity, g/(g·h)
Silica, 500°C	0
2% Al/silica, 500°C	1700
Phosphate silica, ^a 500°C	1500
H_2SO_4 /silica, 300°C	170
Bi/silica, 500°C	410

^aSilica was treated with POCl_3 at 200°C , then H_2O vapor to remove chloride, before final calcining at 500°C .

TABLE 2. Catalyst Activity: $\text{Cr}_4(\text{TMSM})_8$ Injected into Reactor with Isobutane and Various Carriers^a

Carrier	Activity, g/(g·h)
Silica, 800°C	300
Silica, 400°C	400
Alumina, 600°C	1500
Aluminophosphate, 600°C	1000
Fluorided alumina, 600°C	5400
F-Si-alumina, 600°C ^b	8900

^a $\text{Cr}_4(\text{TMSM})_8$, 0.05 mmol; isobutane, 1 L; carrier, 0.05-0.1 g.

^bImpregnated with NH_4HF_2 and $\text{Si}(\text{OEt})_4$ before calcination to equal 1.5% F and 3.2% SiO_2 .

Other organo-Cr compounds, like $\text{Cr}_4(\text{TMSM})_8$ or $\text{Cr}(\text{DMPD})_2$, show similar preferences. Table 2 lists the activity obtained from various supports when contacted with $\text{Cr}_4(\text{TMSM})_8$ in the reactor. Table 3 shows similar trends from $\text{Cr}(\text{DMPD})_2$ impregnated onto different carriers and then introduced into the reactor. Again in both cases silica is a poor support compared to the others. Perhaps this is because the hydroxyls on silica are not very acidic. Alumina

TABLE 3. Catalyst Activity: $\text{Cr}(\text{DMPD})_2$ Impregnated onto Various Carriers

Carrier	Activity, g/(g·h)
Silica, 700°C	100
Aluminophosphate, 600°C	2000
Alumina, 600°C	3900
H_3PO_4 /alumina, 600°C ^a	7000

^aImpregnated with H_3PO_4 in alcohol to equal 0.1 P/Al after calcining.

and aluminophosphates do better. Treating the alumina with fluoride, silica, or phosphate, all of which could enhance acidity, further improves the polymerization activity.

Organo-Cr catalysts, unlike Cr oxide/silica, usually exhibit no induction time. On contact with ethylene, polymerization begins immediately. A typical kinetic profile is shown in Fig. 2. Since they generally start with a low valence, a reduction step is unnecessary. The initial alkylation step, which further contributes to the gradual rise in polymerization rate over Cr oxide/silica, again seems to occur very rapidly on the organo-Cr catalysts, giving a different kinetic profile.

In some cases, such as bisarene Cr(0), these catalysts must be alkylated by ethylene in a process similar to that over Cr oxide. But in other cases, like Cr(TMSM)₄, the catalyst might be considered as already alkylated, i.e., ethylene could insert into a previously existing Cr-TMSM σ -bond. Whether or not this second possibility actually occurs is uncertain.

Beta-H elimination is still a major mechanism of chain transfer on the organo-Cr catalysts. Table 4 shows that the polymer from Cr(DMPD)₂ without H₂ contains approximately an equal number of methyl and vinyl end groups, as is also the case for the products of oxide catalysts. When H₂ is added, however, there is a major response, i.e., an increase in melt index, and this is quite different from Cr oxide/silica. Table 4 also shows that as H₂ is added, the polymer becomes more saturated, indicating that chain transfer now also includes some hydrogenation of chains (Scheme 4).

The sensitivity to H₂ also depends on which carrier is used. The increases in melt index by H₂ are more pronounced when the support contains phosphate, but as shown in Table 4 both *t*-vinyl and methyl end groups seem to be increased by H₂. This phenomenon was also observed from dicumene Cr(0) on aluminophosphate. Apparently then, H₂ can also accelerate beta-H elimination [7, 29].

In fact, the large change in melt index on aluminophosphate does not seem to agree with the relatively smaller change in end groups. We suspect that H₂ preferentially affects the high-MW portion of the distribution, which strongly influences flow properties. The SEC traces in Fig. 4 show two peaks which



SCHEME 4.

TABLE 4. H₂ Response of Cr(DMPD)₂ on Various Carriers

Catalyst	H ₂ , atm	MI ^a	HLM ^a	<i>t</i> -Vinyl ^b	Methyl ^b	Me/Vin ^b
Cr(DMPD) ₂ on alumina, 600°C (P/Al = 0)	0	0	0.03	2.1	2.0	1.0
	6.8	0	1.64	2.0	3.0	1.5
	13.6	0.02	6.11	1.9	3.9	2.1
Cr(DMPD) ₂ on H ₃ PO ₄ /alumina, 600°C (P/Al = 0.1)	0	0	0.01	—	—	—
	6.8	0.52	91	2.3	5.6	2.4
	13.6	2.60	350	—	—	—
Cr(DMPD) ₂ on aluminophosphate, 600°C (P/Al = 0.9)	0	0	0.64	5.5	5.6	1.0
	6.8	24	HIGH	6.3	6.3	1.1
	13.6	47	HIGH	6.7	7.3	1.1

^aMI = melt index, HLM^a = high-load melt index.^bMethyl and *t*-vinyl determinations made by infrared and reported as end groups per 1000 CH₂.

we attribute to two populations of Cr centers. One type, producing high-MW polymer, is associated with surface aluminum and seems to be more sensitive to H_2 . The second type is associated with surface phosphate and produces lower-MW polymer. In contrast, the oxide catalysts typically display only one broad SEC curve.

The MW distribution obtained from organo-Cr catalysts is typically so broad that olefins and liquid oligomers are often produced along with high polymers. For example, $Cr(DMPD)_2$ on $600^\circ C$ silica yields about 75% liquid product. However, this drops to less than 10% liquid product on $400^\circ C$ silica, where the hydroxyls are more closely spaced. The SEC trace in Fig. 4 again shows two peaks, one of which represents the liquid products. Again, it is likely that the two peaks come from reaction of $Cr(DMPD)_2$ with two different types of surface sites, such as isolated versus paired hydroxyls, or even reactive siloxane groups.

The liquid products are always exclusively linear α -olefins of even carbon number. Branched or secondary olefins are not usually found under slurry polymerization conditions.

Possibly as a consequence of these olefins, the high polymers obtained from many organo-Cr catalysts contain a significant amount of branching. The olefins may copolymerize with ethylene to yield branching. The presence of methyl groups can only be explained as isomerization, because propylene is not found in the reactor.

Typically, the amount and type of branching varies with the support employed. Table 5 lists a few examples. The resin density varies widely, tending to be high (>0.960 g/mL is typical of linear polymers) when the support is alumina and low when aluminophosphate or silica is used. Branching seems to be enhanced by a "bare" support like silica which has fewer surface hydroxyls or other coordinating ligands. The same trend toward lower density is observed from a single support as it is progressively dehydrated at higher calcining temperatures.

The decreased resin density obtained from the organo-Cr catalysts agrees with the amount of branching found. Copolymers from Cr oxide display a similar profile of density vs branching. However, the stiffness of the resins produced by organo-Cr is much lower than expected from the density. The flexural modulus of the two resin families is plotted against the density in Fig. 5. In both cases stiffness decreases with density as expected, but two different lines are formed. Exactly why the organo-Cr resins are less stiff (or more dense) after molding is not clear. It may be due to the extremes of the broad MW distribution.

TABLE 5. Typical Branching Patterns from Various Carriers

Catalyst	MI	Resin density, g/mL	Methyl ^a	Ethyl ^a	Butyl ^a
Cr ₄ (TMSM) ₈ /AlPO ₄ , 400°C	0	0.9535	—	—	—
Cr ₄ (TMSM) ₈ /AlPO ₄ , 600°C	39	0.9405	0.14	0.11	0.12
Cr ₄ (TMSM) ₈ /F-alumina, 600°C	11	0.9653	0.15	0.06	0.04
Cr ₄ (TMSM) ₈ /silica, 800°C	0.2	0.9441	0.26	0.40	0.29
Cr(DMPD) ₂ /alumina, 700°C	6	0.9640	0.18	— 0.07	—
Cr(DMPD) ₂ /AlPO ₄ , 600°C	6	0.9490	0.12	— 0.02	—
Cr oxide/silica, 700°C	0.8	0.9600	0	0.02	0.03
Cr(CUM) ₂ /AlPO ₄ , 600°C	—	—	0.10	— 0.24	—

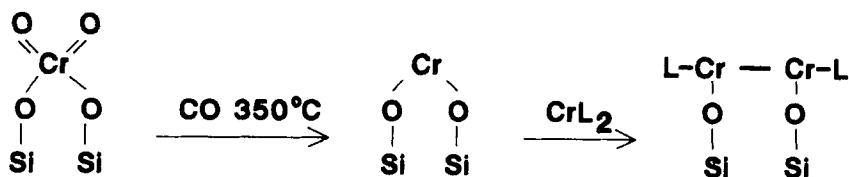
^aBranches determined as mole percent by C-13 NMR.

Mixed Organo/Oxide Chromium Catalysts

Organo-Cr compounds can be reacted with a support like silica as previously described, or alternatively with Cr oxide/silica. This "mixed" catalyst is also very active for ethylene polymerization and, in many ways, is a hybrid, exhibiting some of the characteristics of both its parents [8, 9].

Exactly what happens when the organo-Cr component is added is unclear. It could react with residual surface hydroxyls, but the Cr(VI) oxide, a strong oxidant, is expected to be more reactive. Most likely, it is reduced by the organo-Cr, which in turn acquires oxide bonds, either to the support or to form a Cr—O—Cr pair. Each organo-Cr compound produces a catalyst slightly different in its polymerization behavior, which might be expected, considering the wide variation in organo-Cr compounds. The product species are no doubt highly complex, but appear to be very active.

It is also possible to prereduce the oxide to Cr(II) with CO at 350°C. This material also provides an active catalyst when treated with organo-Cr compounds. However, since there is no redox possibility in this case, one can make a guess at the resultant species. The initial Cr—O—Si link to the support may be attacked, leaving a Cr—Cr pair of some kind. Again, surface hydroxyls may also react with the organo-Cr, and this may be more likely in the absence of Cr(VI) (Scheme 5).



SCHEME 5.

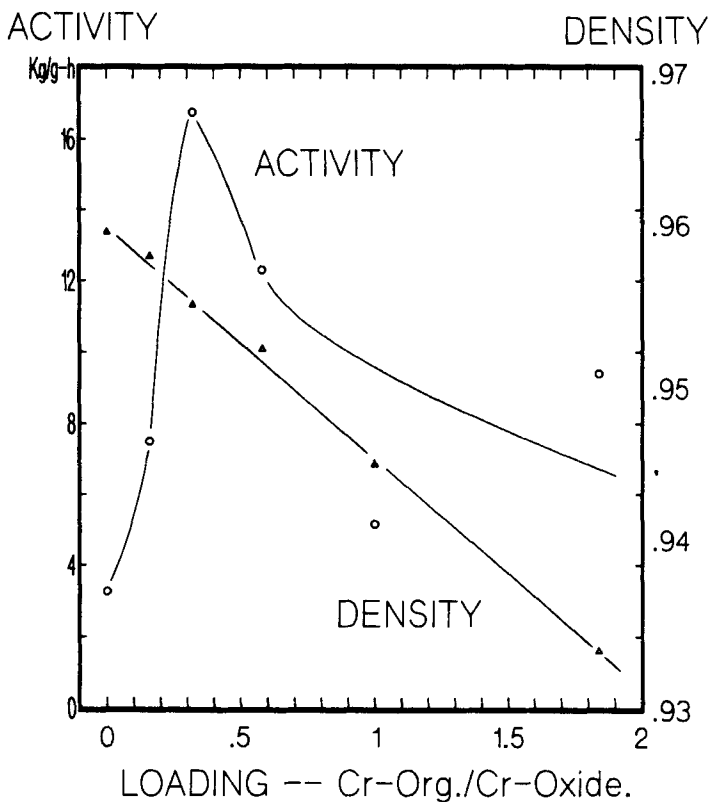


FIG. 6. Activity of the mixed catalyst ($\text{Cr}_4(\text{TMSM})_8$ with Cr oxide/silica) goes through a maximum as the organo-Cr loading is increased. The density of resins from the mixed catalyst also depends on how much organo-Cr compound is used to make the catalyst. The higher the loading, the lower the density.

TABLE 6. Impregnation of a Hexavalent and a Zerovalent Organo-Cr Compound onto Calcined Silica

<i>t</i> -Butyl CrO ₄ , %	Cr(CUM) ₂ , %	Activity, g/(g·h)
1.0	0	0
1.0	0.5	0
0.5	0.5	700
1.0	1.5	2140
0	1.0	0

The activity of these mixed catalysts is usually higher than that of either individual component. For example, Fig. 6 shows the activity of Cr oxide/silica increasing and going through a maximum as the loading of the organo-Cr component, Cr₄(TMSM)₈, increases. Another example is provided in Table 6. Deposited on silica at 40°C, *t*-butyl chromate is inactive, as is dicumene Cr(0), but together they react to form an active catalyst. Both cases argue against the organo-Cr merely reacting with surface hydroxyls, which would not significantly enhance the activity, since silica is a poor carrier for organo-Cr compounds. Instead, the active complex must involve some type of joint Cr—Cr reaction product. Too much organo-Cr may completely sever the original oxide bonding, hence the maximum in Fig. 6. Other metal alkyls, such as AlR₃, also tend to kill Cr oxide/silica when added in excess to the reactor.

The fact that the two Cr components react with each other is further supported by the kinetic profile of the mixed catalyst. The induction time was shortened by Cr₄(TMSM)₈, as would be expected when any metal alkyl is added, but the kinetics did not resemble that of the supported organo-Cr catalysts. Instead, the activity gradually increased during the run, as is typical of the oxide. This rise has been attributed to an alkylation reaction.

Thus a redox reaction seems to occur between the two Cr species, probably leaving a complex in which the Cr oxide is left in a reduced state. The induction time is shortened, but alkylation is still required.

In other characteristics of the mixed catalyst, the oxide component also seems to dominate. For example, the mixed catalyst, unlike the organo-Cr catalysts, is not highly sensitive to H₂. Its response lies between the two extremes, depending on the organo-Cr loading, but is usually closer to that of the oxide parent.

TABLE 7. Cr(II) versus Cr(VI) Oxide on Silica^a

Valence of oxide	Organo-Cr/Cr oxide	Resin density, g/mL
+6	0.5	0.9552
+6	1.0	0.9483
+6	1.5	0.9382
+2	0.5	0.9406

^aCr₄(TMSM)₈ was impregnated onto Cr oxide/silica at various loadings. In one case the oxide was CO-reduced to yield Cr(II).

The organo-Cr component, however, does play an important role in the mixed catalyst. That it serves as more than just a reducing agent for the oxide is clear from the density of the resins produced. Whereas the oxide yields linear homopolymers, the mixed catalysts produce branched polymers, like the organo-Cr catalysts. Resin density can be depressed from 0.960 g/mL, which is typical of homopolymers, to the 0.920 g/mL range, depending on the loading of the organo-Cr component. This is shown in Fig. 6. The more organo-Cr compound added to the oxide catalyst, the lower the resin density.

The oxide precursor can be prereduced in CO to yield Cr(II) instead of the usual Cr(VI) oxide, and then needs no further reduction in the reactor. This makes the organo-Cr component even more effective at lowering the resin density, as shown in Table 7. Apparently less of it is consumed by the oxide as a reductant. The resultant Cr—Cr complex may thus be a little different when Cr(II) oxide is used, but again it is seen that the organo-Cr component is an active participant in the mixed catalyst, more than just a reducing agent.

The effectiveness of the mixed catalyst at lowering the resin density also depends on which organo-Cr compound is used (see Table 8). For a given loading, the divalent chromium alkyl Cr₄(TMSM)₈ is especially effective.

The type of branching found in the resin also varies with the organo-Cr compound used, but is predominately in the C₂ to C₆ range. The corresponding C₄ to C₈ olefins are detected in the reactor, usually in a similar ratio to that of the branching. In fact, the more olefins found in the reactor, the lower the density of the resin produced (for an example, see Fig. 7). The density of the resin, compared to the amount of olefins found in the reactor, is consistent with copolymerization by straight Cr oxide/silica in which olefins are added rather than self-generated (See Table 9). Thus, it seems likely that olefins are formed and then incorporated as branches into high polymers.

TABLE 8. Efficiency of Various Organo-Cr Compounds

Organo-Cr compound	Loading, org/ox	Activity, g/(g·h)	Resin density, g/mL
Cr(cumene) ₂	1.0	6,400	0.9529
Cr(DMPD) ₂	1.0	10,900	0.9616
Cr ₄ (TMSM) ₈	1.5	8,800	0.9562
Cr ₄ (TMSM) ₈	1.0	3,900	0.9471
Cr(benzene) ₂	1.5	4,760	0.9520
Cr(octoate) ₃	0.5	1,120	0.9601

TABLE 9. Branching Distribution from Cr₄(TMSM)₈ Mixed Catalysts^a

Loading, org/ox	Resin density, g/mL	Olefins in reactor			Branches in polymer		
		C ₄	C ₆	C ₄ /C ₆	C ₂	C ₄	C ₂ /C ₄
0.8	0.9435	0.40	0.32	1.25	0.36	0.25	1.44
0.8	0.9383	0.37	0.38	0.97	0.49	0.53	0.92
0.8	0.9389	0.40	0.36	1.11	0.61	0.66	0.92
0.8	0.9364	0.63	0.50	1.26	0.72	0.61	1.18
0.5	0.9500	0.03	0.15	0.20	0.09	0.29	0.31
0.5	0.9489	0.02	0.11	0.18	0.12	0.32	0.38
0.5	0.9457	0.06	0.45	0.13	0.23	0.52	0.44
0 ^b	0.9380	0	0.70	0	0	1.80	0

^aOlefins and branching reported as mole percent of ethylene.

^bHexene added to reactor.

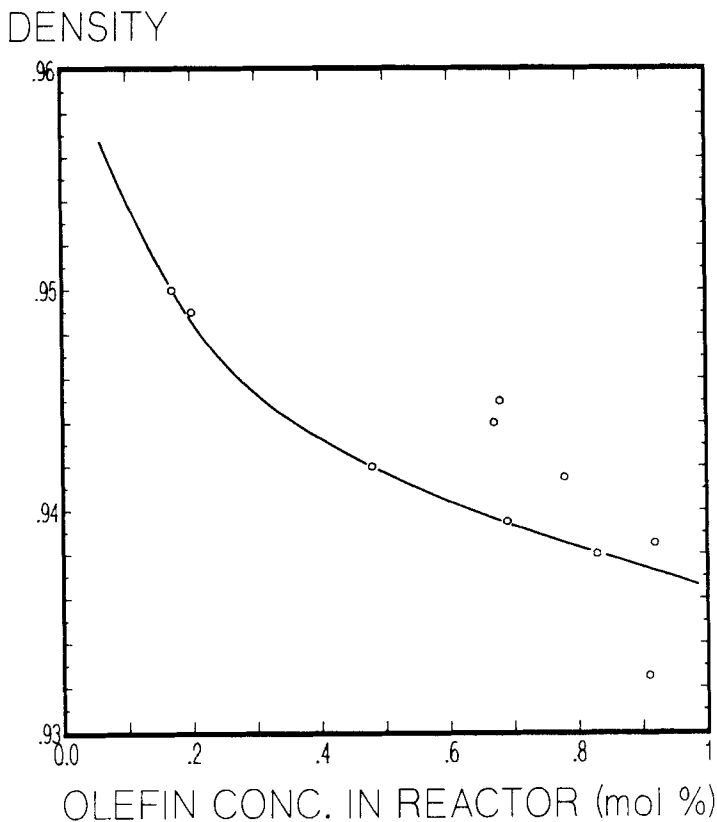


FIG. 7. Product density as a function of olefin concentration in the reactor. In addition to high polymers, the mixed catalyst also produces liquid olefins. The more olefins generated, the lower the density of the high polymer. This suggests that the olefins are incorporated as branches into the polymer chains.

Methyl branches are sometimes also detected in the polymer, but propylene has never been found in the reactor. Thus methyl branching at least must be formed by isomerization. The mixed catalysts produce a lower level of methyl branching than organo-Cr on the same support (see Table 10).

The distribution of olefins produced by the mixed catalysts, or the distribution of branches found in the polymer, does not seem to fit the conventional

TABLE 10. $\text{Cr}_4(\text{TMSM})_8$ on Silica or Cr oxide/Silica^a

Properties	Silica	Cr oxide/silica
SEC \bar{M}_w	274,000	248,000
NMR \bar{M}_n	1,600	8,500
\bar{M}_w/\bar{M}_n	175	29
Density, g/mL	0.944	0.940
NMR branching:		
Methyl, mol%	0.22	0
Ethyl, mol%	0.44	0.56
Butyl, mol%	0.19	0.50

^a $\text{Cr}_4(\text{TMSM})_8$ was impregnated onto two silica carriers, one containing Cr oxide and one not.

Schultz-Flory distribution. In fact, 1-hexene is often generated in the highest concentration, as can be seen in Table 9. Again, $\text{Cr}_4(\text{TMSM})_8$ is a particularly effective organo-Cr compound, producing a rather narrow cut of olefins. In Table 11 it is compared to dicumene Cr(0). Even for a given organo-Cr compound, the distribution of olefins (or branches) can be influenced by reactor and other variables. For example, increasing reactor temperature seems to favor hexene production, relative to butene, while H_2 has the opposite effect.

TABLE 11. Comparison of Olefin Distribution Produced by Two Organo-Cr Compounds in the Mixed Catalyst^a

Organo-Cr compound	Resin density, g/mL	Olefins in reactor			
		C_6 , mol%	C_8 , mol%	C_{10} , mol%	C_{12} , mol%
$\text{Cr}(\text{cumene})_2$	0.945	0.97	0.31	0.27	0.13
$\text{Cr}_4(\text{TMSM})_8$	0.939	0.52	0.10	0.03	0
$\text{Cr}_4(\text{TMSM})_8$	0.952	0.16	0.03	0	0

^aCarrier was Cr oxide/silica; organo-Cr loading was 1.5 Cr/Cr.

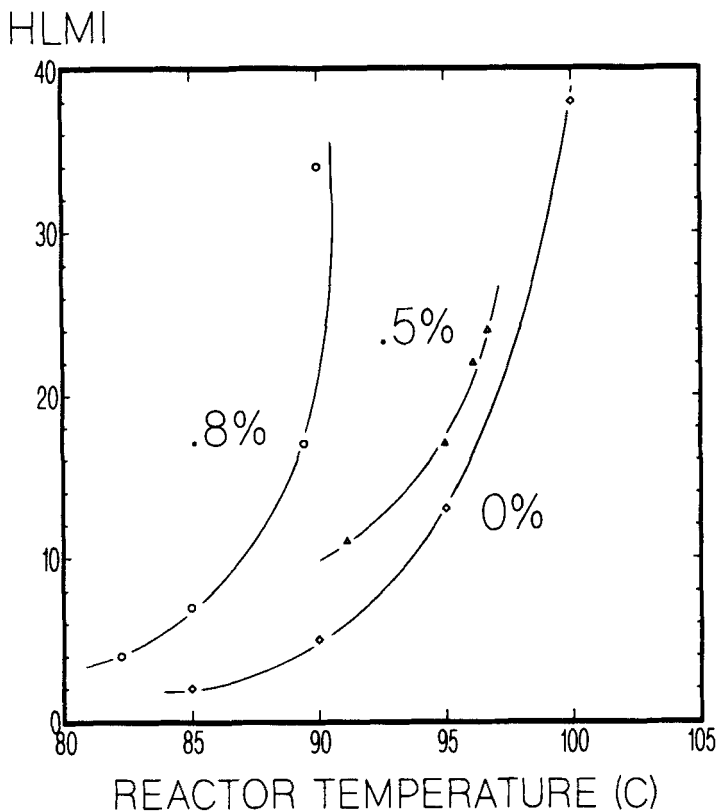


FIG. 8. Chain transfer, shown here by the high load melt index (HLMI), is enhanced by increasing the reactor temperature for the mixed catalyst as well as for Cr oxide. Three loadings of $\text{Cr}_4(\text{TMSM})_8$ are shown: 0.8% Cr, 0.5% Cr, and 0% Cr. The higher the organo-Cr loading, the higher the melt index potential.

The most significant influence may be the loading of the organo-Cr compound; low loadings favor hexene. Some examples are shown in Table 9.

In many other characteristics of the mixed catalysts, however, they behave like their oxide parents. Melt index is still controlled primarily through reactor temperature. Figure 8 shows this trend for three different loadings of $\text{Cr}_4(\text{TMSM})_8$. In each case the melt index of the resin produced increases exponentially with reactor temperature. However, the process is accentuated by the organo-Cr component. This probably merely reflects the density suppres-

TABLE 12. Summary

	Cr oxide	Organo-Cr	Mixed Cr
Induction time	Yes	No	No
Kinetics	Increasing	Decreasing	Increasing
Activity on silica	High	Low	Very high
H ₂ sensitivity	Low	High	Intermediate
MW distribution	Moderate	Broad	Intermediate
Methyl branching	None	High	Low
Other branching	None	High	High
Stiffness	High	Low	Intermediate

sion by organo-Cr. Oxide catalysts exhibit a similar melt index increase when olefins are intentionally fed to the reactor to create branching.

The molecular weight distribution of the resin properties from the mixed catalysts also resemble those of oxide catalysts. \bar{M}_w/\bar{M}_n values typically varied from 10 to 30, depending on the carrier. $\text{Cr}_4(\text{TMSM})_8$ produces a much broader MW distribution when impregnated onto silica than when impregnated onto Cr oxide/silica, even though approximately the same density results (Table 10). Figure 5 shows the stiffness-density relationship of such resins. For a given density they are intermediate in stiffness between the straight oxide or organo-Cr parents. On the whole, the blow molding and film characteristics are competitive with, and in some cases superior to, conventional hexene copolymers from Cr oxide/silica.

CONCLUSIONS

The mixed catalysts act like hybrids, possessing some of the characteristics of both parents, as summarized in Table 12. Many of these characteristics (for example, the activity of the mixed catalyst or its kinetic profile) are not simple combinations of the two parents; instead, they are genuinely different. This suggests that new species, probably complex, are produced through a redox reaction between the Cr oxide and the organo-Cr reducing agent.

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